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TECHNICAL NOTE 2380

EFFECTIVENESS OF CERAMIC COATINGS IN REDUCING CORROSION OF FIVE HEAT-RESISTANT ALLOYS BY LEAD-BROMIDE VAPORS

By Dwight G. Moore and Mary A. Mason

National Bureau of Standards



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SUMMARY

Lead compounds in the combustion products of high-octane fuel have been suspected of being a contributing factor in causing failures of the heat-resistant alloy parts in aircraft exhaust systems. The principal lead compound present in the exhaust gases is lead bromide $PbBr_2$ and it was desirable to determine whether this compound, which is present in the vapor state at operating temperatures, could be corrosive toward these alloys under laboratory test conditions. It was also desirable to find out whether ceramic coatings, which have been used successfully on some aircraft exhaust parts, were protective against such corrosion as might occur under these conditions.

To obtain these answers for five heat-resistant alloys, a test was devised in which the alloy specimens (a) in an uncoated condition, (b) in a preoxidized condition, and (c) with three different ceramic coatings were exposed for 6 hours to $PbBr_2$ vapors in an air atmosphere at temperatures of 1350°, 1500°, and 1650° F. Under these conditions, a fairly rapid corrosion accompanied by a loss of thickness occurred on both the uncoated and preoxidized alloys, but on the specimens that were ceramic-coated no significant attack took place.

The results may be summarized as follows:

(1) Large differences in the resistances of the several alloys to attack by $PbBr_2$ were noted, alloys S-816, H.S. 21, and Inconel being more resistant than the two chromium-nickel, austenitic-type stainless steels, 19-9DL and AISI Type 347

(2) Preoxidation of the alloys prior to test tended to retard the corrosive action of $PbBr_2$ for a short time, after which the attack proceeded at about the same rate as for the uncoated specimens

(3) Ceramic coatings appeared to be inert to the $PbBr_2$ fumes and thus successfully inhibited corrosion of the alloys for the full 6-hour test period

INTRODUCTION

Lead bromide $PbBr_2$ is present in the exhaust gases from all engines that use a leaded gasoline as fuel. The lead is added to the fuel as tetraethyl lead and at the same time ethylene dibromide is introduced. The purpose of the ethylene dibromide is to act as a scavenging agent, that is, to convert the lead oxide, which would otherwise be formed during combustion, into $PbBr_2$, which has a considerably higher vapor pressure than lead oxide and is therefore more easily passed through the exhaust system as a vapor.

The effect of $PbBr_2$ fumes on the corrosion rate of heat-resistant alloys at elevated temperatures has been investigated, but there is no accepted consensus whether the effect on the alloys currently used for aircraft exhaust systems is significant. A few exploratory tests, made at the National Bureau of Standards using $PbBr_2$ vapors in air at 1500° F, indicated that the alloys under these conditions were appreciably attacked. Further, these exploratory tests showed that a ceramic coating successfully inhibited the corrosion. These results warranted additional work and the present report gives the data obtained from the more complete study.

The investigation as herein reported was carried out at the National Bureau of Standards under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

The authors wish to express their grateful appreciation to Mr. W. N. Harrison, under whose direction the study was conducted, for his helpful suggestions throughout the investigation and also to Mr. J. W. Pitts who prepared the metallographic sections.

LITERATURE REVIEW

A literature survey indicated that studies of corrosion by $PbBr_2$ had been confined essentially to the effect of deposits on combustion chambers, spark plugs, and valves (references 1 to 3). There have been very few publications on the corrosion effects of lead compounds upon exhaust disposal systems. One of the earliest reports was published in 1930 by Heron (reference 4). This work, which was reported shortly after the adoption of leaded gasoline by the United States Air Corps, involved burning leaded and unleaded gasolines in blow torches, the flame being passed through pipes $1\frac{1}{2}$ inches in diameter and 24 inches long. The test was of 20 hours' duration and during this period a 6-inch zone of the pipe was maintained at a "red heat." Under these

test conditions, slightly more scale was formed on mild steel pipes with the leaded fuel than with the unleaded fuel. In addition, the scale formed with the leaded fuel was decidedly less adherent than that formed with unleaded fuel and it tended to blow out of the discharge end of the pipe during test.

In other tests reported by Heron the ethylene-dibromide content of the gasoline was retained but no tetraethyl lead was present. In this case, the attack was the same as for the fuel containing neither addition, indicating that the presence of tetraethyl lead in the gasoline had been responsible for the observed increase in attack. Because of this finding, Heron believed it desirable to determine the corrosion effects of $PbBr_2$ on various alloys at elevated temperatures in an air atmosphere. In this work, 0.3 gram of $PbBr_2$ was placed on the surface of each specimen, and the specimens were then heated in air for 2 hours in the range of 700° to 1000° F. The amount of attack, which was estimated by visual examination, varied over a wide range, depending on the alloy. Other tests were made in which $PbBr_2$ was dropped on the surface of the alloy, maintained at a red heat. In discussing these latter tests Heron states that, while such treatments are probably "too drastic," the results are nevertheless in general accord with tests on tubes and experience with various materials in service.

Kirtchik (reference 5), in studying the intergranular corrosion that occurs on exhaust-system supercharger nozzle boxes, concluded that the attack was caused by the combination of water and lead halide on the surface of the alloy. The water is formed by condensation from cooled exhaust gases or from the atmosphere during periods in which the aircraft is inactive, while the $PbBr_2$ is deposited during engine operation. The attack occurs during subsequent heating. According to Kirtchik's experiments lead-halide fumes, by themselves, do not attack the heated alloys and, also, lead halide in water solution does not attack the alloys at ordinary room temperature.

Wilkes (reference 6), after studying stress-corrosion of turbosupercharger alloys in the products of combustion of leaded gasoline, postulated that the corrosion might be due to lead oxide PbO alone, the magnitude of attack depending on whether or not it is molten. According to Wilkes, the $PbBr_2$, which is also present in the exhaust gases, might greatly aid the production of a PbO-bearing liquid deposit.

Heron, Harder, and Nestor (reference 7), in discussing the high-temperature scaling of exhaust-valve alloys, state that corrosion by vapors of lead compounds appears to be unimportant. However, these same authors also state that, while some of the exhaust-valve materials of relatively low alloy content form surface films which are inert to most of the products of combustion, the same alloys are exceedingly reactive with the combustion products of lead antiknock fluid. These combustion

products, according to the authors, are lead halides, lead oxyhalides, lead oxide, and lead sulfate.

In 1946, Heron (reference 8), in discussing the operating difficulties of aircraft engines with fuels containing tetraethyl lead, states that "the pipes, ducts, etc. carrying the exhaust gases from the cylinders to the atmosphere (often via an exhaust gas turbine driving a supercharger) are attacked by lead compounds if the material (from which the pipes, ducts, etc. are made) is unsuitable or if the operating temperature is too high."

MATERIALS

Alloy specimens.- Five alloys were included in the present study, namely, AISI Type 347 and 19-9DL stainless steels, Inconel, S-816, and H.S. 21. Representative compositions of the five alloys are given in table 1.

The specimens, which were sheared from 18-gage sheets, were $\frac{1}{2}$ inch wide by $1\frac{1}{2}$ inches long with a $\frac{5}{32}$-inch hole centered near one end. The specimens were cleaned by a light sandblast and then divided into 5 sets of 30 specimens each. One of these sets was tested with no further treatment, a second set was preoxidized for 4 hours in air at the test temperature, and the other three sets were ceramic-coated.

Coatings.- The three ceramic coatings selected for test were prepared by the National Bureau of Standards and designated A-417, A-19, and A-520. These coatings, which are all being used commercially, were applied to the specimens by dipping, after which they were bonded to the alloy by firing to the proper maturing temperatures. The average thicknesses after firing were 0.0017 inch for A-417, 0.0042 inch for A-19, and 0.0012 inch for A-520.

The compositions of the three coatings, together with the details of application, are given in table 2.

EXPERIMENTAL PROCEDURE

The test method employed in the present study involved the use of the furnace shown diagrammatically in figure 1. In performing a test, the furnace was first heated to one of the selected temperatures (1350°, 1500°, or 1650° F) and allowed to come to equilibrium. The lid was then removed and 1 gram of chemically pure $PbBr_2$ was charged into the furnace

before a second lid, with eight specimens suspended as shown in figure 1, was quickly put into position. The charging was done in such a way that only the vapor form of the $PbBr_2$ could come into contact with the specimens during the 1-hour heating period. The temperature was controlled to $\pm 7^{\circ}$ F.

After this heating period, the specimens were removed from the furnace and the bottom $\frac{1}{4}$-inch strip of each specimen was sandblasted[1] to remove the ceramic coating or the scale, as the case might be. The thickness of metal at this area was then determined with a micrometer. The decrease in alloy thickness caused by the type of sandblast required to remove the scale was found in each case to be less than 0.2 mil.

After completing the thickness measurements, the same specimens were placed in the furnace for a second treatment under conditions identical with those of the first treatment. At the conclusion of the 1-hour heating, they were removed and a second $\frac{1}{4}$-inch strip adjacent to the first strip was cleaned for thickness measurements. This procedure was repeated four additional times, or until 6 hours of treatment had been accumulated.

In most cases duplicate specimens were employed. However, for Inconel, in the unoxidized and preoxidized condition, six specimens were used in order to establish better the effect of testing time on the protective properties of the preoxidized layer.

During any of the 1-hour treatments, the $PbBr_2$ concentration in the furnace atmosphere was high immediately after the specimens were inserted but the concentration undoubtedly diminished with time. The furnace was so constructed that air circulation was limited, air entering for the most part through the thermocouple hole at the bottom and leaving through the holes in the loose-fitting lid at the top. Inasmuch as the purpose of the tests was to determine the effectiveness of ceramic coatings in preventing $PbBr_2$ attack, no attempts were made to control concentrations within the furnace other than to use the same furnace throughout and to standardize both the method of charging the $PbBr_2$ and the method of inserting the specimens into the furnace.

RESULTS

Figure 2 shows the appearance of coated, uncoated, and preoxidized specimens of AISI Type 347 stainless steel after 6 hours' treatment

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[1]The sandblasting was done with 60-mesh glass sand and with an air pressure of 80 psi.

at 1650° F. For this particular test, the specimens were left in the furnace continuously for the 6-hour period at 1650° F. Hourly charges of 1 gram of $PbBr_2$ were made through an alloy tube inserted into a hole in the lid. In this way the $PbBr_2$ was prevented from coming into contact with the specimens until it was in the vapor form. As can be seen in the photograph, nearly all of the scale flaked from the uncoated and preoxidized specimens after cooling, whereas only a very mild flaking of the A-417 coating occurred near areas of poor initial coverage at the top and bottom edges.

Loss in weight.- Under the test conditions used, the scale that formed on most of the alloys could not be completely brushed free of the alloy. In the case of Inconel that had been treated at 1500° F it was found that scale removal could be readily accomplished by brushing, and hence loss-in-weight determinations were made for a few Inconel specimens. Figure 3 shows the loss in weight of this alloy plotted against time of treatment in the $PbBr_2$ atmosphere at 1500° F as compared with the same alloy with coating A-417. No significant weight change was noted for Inconel coated with A-417 after exposure to the $PbBr_2$ vapors for 6 hours, but in the same period the uncoated Inconel lost about 160 milligrams per square centimeter of exposed surface.

Loss in thickness.- The loss-in-thickness data for the five alloys after exposure for 6 hours to the $PbBr_2$ vapors in an air atmosphere at the three test temperatures are given in table 3. These data include the average thickness losses for the uncoated specimens, the preoxidized specimens, and the specimens protected with various ceramic coatings.

Figures 4 to 6 show the average thickness loss plotted against treatment time at each of the three temperatures for uncoated AISI Type 347 stainless steel and for both the uncoated and preoxidized specimens of Inconel.

Spectrochemical analyses.- Spectrochemical analyses were made of scale collected from uncoated specimens of each alloy after exposure to the $PbBr_2$ vapors in air at 1500° F. Table 4 gives the results of these analyses together with the analyses of the alloy surfaces which had been cleaned of all remnants of adhering scale by a light sandblast.

Microstructure.- Figures 7 and 8 show the microstructure of uncoated specimens of all five alloys after 6 hours' treatment at 1500° F.

DISCUSSION OF RESULTS

Table 3 shows that, although the uncoated and preoxidized specimens of all five alloys were attacked by the $PbBr_2$ vapor in an air atmosphere

at all three test temperatures, there was nevertheless considerable variation in the degree of attack. Of the five uncoated alloys without preoxidation, S-816 and Inconel showed the best resistance at 1350° F, H.S. 21 at 1500° F, and Inconel at 1650° F. The uncoated and preoxidized specimens of AISI Type 347 and the 19-9DL stainless steels were notably less resistant to the test conditions at all test temperatures than were the other three alloys.

Ceramic coatings in all cases were effective in inhibiting the alloy attack by the $PbBr_2$ vapor. Although there appeared to be no significant difference among the three coatings in this respect, there was a tendency for the A-19 and the A-520 to lose adherence on the AISI Type 347 and the 19-9DL stainless steels, especially at the 1650° F test temperature. The A-417 did not show this effect except near those areas where the initial coverage had been poor.

Table 3 also shows that the average decrease in thickness of the coated specimens was 1.1 mils or less in all cases. Microscopic examination of sections, on the other hand, indicated no loss of thickness. Thus, it is believed that the necessity for a sandblast treatment to remove the coating was responsible for the small losses recorded for the coated specimens. In the case of the uncoated specimens, the scale came off easily, and therefore reduction in metal thickness by the light sandblast that was required did not significantly affect the loss-in-thickness measurement.

In most of the tests the corrosion of the alloys was of a pitting type, making accurate thickness measurements difficult. A ball-probe micrometer was used to reduce errors from this source. The small $\left(\frac{1}{16}\text{-in.-diam.}\right)$ probe penetrated the pits and, by taking three readings across the specimen with the ball-probe micrometer and one reading with a regular micrometer having a flat face, an arbitrarily weighted average was obtained.

It will be noted that the data in table 3 (and figs. 4 to 6) do not show any consistent tendency toward increased corrosion with increased temperature. Indeed, in a number of cases, the opposite trend is shown. Such results are not unusual in corrosion studies of alloys and, in fact, one example of greater attack by the products of combustion of leaded fuels at low temperature than at high temperature was observed by Heron (reference 4) for calorized low-carbon steel. Heron reported that there was no attack by the lead compounds on the calorized tubes used in the blow-torch tests in the hot zone, yet the discharge end of the tube, which operated at a lower temperature, showed a fairly heavy formation of loose, rusty scale. In the present work, greater attack was noted at 1500° F for the uncoated and preoxidized specimens of

Inconel, H.S. 21, and S-816 than was found at 1650° F, while the other two alloys, 19-9DL and AISI Type 347, showed about the same attack at these two temperatures.

Before complete acceptance of these test data on the effect of test temperature on the degree of attack, however, it is necessary to consider the possibility that, at the higher temperatures, the concentration of the $PbBr_2$ in the furnace atmosphere probably dropped off more rapidly with time than was the case at the lower temperatures. Wilkes (reference 6) gives the following values for the vapor pressures of $PbBr_2$:

Temperature (°F)	Vapor pressure (mm of Hg)
1200	11
1500	200
1680	760

Thus, at 1650° F, it is possible that the 1-gram charge of $PbBr_2$ would leave the furnace in a matter of minutes while at 1350° and 1500° F the same 1-gram charge would be feeding fumes into the furnace atmosphere for a considerably longer period, or possibly throughout the entire 1-hour heating period. Therefore, it is at least possible that the greater attack at the lower temperatures in the present work may have been caused by these concentration variables.

Figures 4 to 6 show that preoxidation for 4 hours in an air atmosphere at the test temperature tends to retard the attack on Inconel. The shape of the curves indicates that the oxide scale has some protective properties during the first hour or two but that once this protective barrier is penetrated the attack progresses equally as fast as when no oxide scale is present. The ceramic coatings, on the other hand, are apparently resistant to penetration and maintained their effectiveness throughout the entire 6-hour test period. Table 3 shows that the preoxidized specimens had a lower average loss in thickness than the uncoated specimens except for AISI Type 347 and 19-9DL at 1650° F and S-816 at 1350° F.

Figures 7 and 8 show the microstructures of uncoated specimens of the five alloys after the 6-hour treatment at 1500° F. The attack mechanism for uncoated S-816, H.S. 21, and Inconel appears to be mostly a surface corrosion without any appreciable penetration of the corrosion medium into the alloy structure. In the case of AISI Type 347 and 19-9DL stainless steels, however, corrosion by lead compounds has

apparently caused an intergranular type of corrosion, leaving a spongy layer near the surface. Figure 7 shows these two alloys in both the etched and unetched conditions.

It is significant that the spectrochemical analysis (see table 4) shows only a small quantity of lead in the scale from AISI Type 347 and 19-9DL alloys. Inasmuch as AISI Type 347 and 19-9DL show the greatest average thickness losses at 1500° F, it may be concluded that in the case of these two alloys the lead corrosion medium has penetrated into the alloy structure. Heron (reference 4) found that when aluminum sheet was subjected to molten $PbBr_2$ a fairly heavy attack resulted and the scale was adherent. He also found that the $PbBr_2$ was largely reduced to metallic lead. According to Graham (reference 9), who noted a similar reduction beginning at temperatures as low as 635° F, the $PbBr_2$ reacts directly with the aluminum to form anhydrous aluminum bromide and elemental lead. Although no experimental evidence was obtained, it is conceivable that in this study a similar reduction may have occurred with the two alloys of high iron content, AISI Type 347 and 19-9DL.

The mechanism of the attack by the presence of $PbBr_2$ vapor in an air atmosphere on S-816, H.S. 21, and possibly Inconel is believed to be of a type described in an earlier study at this laboratory on the high-temperature corrosion of various compounds on four heat-resistant alloys (reference 10). The spectrochemical analysis (table 4) showed measurable quantities of lead present in the scales from these three alloys. It is possible that this contaminant could have destroyed the tight, impervious nature of the scale that would normally form and, by so doing, allowed a more rapid oxidation to take place. Also, the retardation of attack during the first hour or two for the preoxidized specimens (see fig. 4 to 6) can be explained by postulating that a certain time is required for the $PbBr_2$ to react with the previously formed scale and cause it to lose its imperviousness.

Wilkes (reference 6) reports that experience with jet-engine combustion chambers showed much greater corrosion if leaded fuels were used. The combustion atmosphere in this case contains a high percentage of oxygen, approaching that of air. Wilkes ascribes this more rapid attack with leaded fuels to the corrosive effects of air plus the accelerating effects of PbO. In the light of the present study, it is believed that $PbBr_2$ in the combustion gases rather than PbO may be the compound causing the accleration.

The findings of Kirtchik (reference 5) that $PbBr_2$ fumes, by themselves, do not cause any significant corrosion of the surfaces of heat-resisting alloys is not in accord with the results of the present study. In Kirtchik's work, pure $PbBr_2$ was distilled out of a small fused-silica

retort and the fumes were allowed to pass over the alloy specimens which were heated in a 10-inch fused-silica tube with a $\frac{1}{2}$-inch inside diameter. The test temperatures were 1100°, 1200°, 1300°, 1400°, and 1500° F. A possible explanation of the fact that only very slight corrosion was noted under these conditions was believed, after correspondence with Mr. Kirtchik, to have been the absence of air in the furnace tube atmosphere. If this belief is correct, then it follows that the presence of an oxidizing atmosphere may be essential for the occurrence of the $PbBr_2$ attack. In any event, further work on the effect of atmosphere is indicated. Another possible explanation for the difference in results (also established by correspondence) was the presence of an oxide film on Kirtchik's specimens. All of his specimens had been annealed at 1950° F followed by cooling in air. These oxide films, as indicated in figures 4 to 6, would have had a tendency to inhibit the corrosive attack for the short test periods used (15 to 20 min).

The concentrations of $PbBr_2$ in the test furnace atmosphere in the present study, while not accurately known, were probably much higher than would be encountered in an aircraft exhaust during routine operation. It is believed possible, however, that under certain conditions relatively high concentrations of $PbBr_2$ in the exhaust gases may be encountered. For example, it may be expected that during low-load engine operation $PbBr_2$ would deposit as a solid on the cooler parts of the exhaust system[2]. Later, when the engine is operated under higher loads, these same parts would become hotter, the deposited $PbBr_2$ would melt (melting point, 698° F), and the vapors would feed into the exhaust stream, thereby increasing, for a short time at least, the $PbBr_2$ concentration in the gases. Also, if part of the deposited $PbBr_2$ were to react with the alloy surface, or the scale, at the temperature at which it deposited, subsequent heating to a higher temperature would be expected to intensify the attack. In this connection, Harder and Nestor, in an unpublished study referred to by Heron, Harder, and Nestor (reference 7), found during experimentation with a products-of-combustion furnace involving temperature cycling of the specimens that lead compounds were deposited during the cooling cycle. Subsequent heating gave much more attack than was obtained by vapor-phase exposure.

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[2]Deposited $PbBr_2$ has been observed in the case of heat exchangers for heavy bombers which were cut from aircraft after being in service for relatively short periods. When these parts were sent for ceramic-coating application, considerable quantities of $PbBr_2$ were found in those parts of the exchanger that would be expected to operate at a relatively low temperature. When the exchanger was heated in a furnace to 1500° F this material melted and vaporized, giving off copious fumes in the process.

Further, the relative order of resistance of a variety of materials tested by this temperature-cycling procedure was found to be much closer to that obtained in normal engine operation than was the case when the test was made at constant temperature.

In the present study no attempt was made to simulate service operation within an exhaust system since the main objective was to determine whether ceramic coatings were capable of inhibiting attack by $PbBr_2$ in an air atmosphere over a temperature range comparable with that encountered in an exhaust disposal system for modern aircraft. The fact that ceramic coatings are being used successfully for exhaust stacks on patrol bombers and for the heat exchangers on heavy bombers indicates that they are also protective against corrosion that may occur under actual service conditions.

SUMMARY OF RESULTS

A study was made of the corrosive attack of lead-bromide $PbBr_2$ vapors in an air atmosphere on five heat-resistant alloys (a) in an uncoated condition, (b) in a preoxidized condition, and (c) with ceramic coatings. The following results were obtained from this investigation:

1. When $PbBr_2$ vapor was present in appreciable concentration at temperatures of 1350°, 1500°, and 1650° F, serious corrosion of the uncoated alloys resulted.

2. Large differences in the resistance of the different alloys to the $PbBr_2$ attack were noted. Uncoated and preoxidized specimens of alloys S-816, H.S. 21, and Inconel were more resistant than the two austenitic stainless steels, AISI Type 347 and 19-9DL.

3. Preoxidation of the alloys prior to test retarded the corrosive attack of the $PbBr_2$ for a short time, after which the attack proceeded at an undiminished rate.

4. The ceramic coatings appeared to be inert to the $PbBr_2$ fumes and thus successfully inhibited the corrosion of all the alloys investigated for the full test period of 6 hours.

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Washington, D. C., June 30, 1950

REFERENCES

1. Droegemueller, E. A.: Cutting Aircraft Maintenance Costs. Bull. No. 148, A.S.T.M., Oct. 1947, pp. 79-86.

2. Droegemueller, E. A.: Better Lead Scavenging Needed for Aviation Gasoline. Bull. No. 154, A.S.T.M., Oct. 1948, pp. 53-56.

3. Downs, D.: Lead Distribution. Auto. Eng., vol. 39, no. 517, Aug. 1949, pp. 304-310.

4. Heron, S. D.: High-Performance Gasoline Aircraft Engine. Its Problems of Fuel, Oil, and Materials of Cylinder Construction. Trans. A.S.M.E., vol. 2, no. 4, 1930, pp. 233-253.

5. Kirtchik, H.: Intergranular Corrosion Determination. The Iron Age, vol. 159, no. 10, March 6, 1947, pp. 67-70.

6. Wilkes, G. B., Jr.: Stress-Corrosion Tests on Turbo-Supercharger Materials in the Products of Combustion of Leaded Gasoline. Symposium on Corrosion of Materials at Elevated Temperatures, A.S.T.M, June 1950. (Special Tech. Pub. No. 108.)

7. Heron, S. D., Harder, O. E., and Nestor, M. R.: Exhaust Valve Materials for Internal Combustion Engines. Symposium on New Materials in Transportation, A.S.T.M. (Detroit), March 6, 1940, pp. 1-26. (Issued as separate pub., STP No. 44.)

8. Heron, S. D.: Monograph - Engine Performance with High Octane Number Fuels. Ethyl Corp., Feb. 1949.

9. Graham, R.: The Effect of Lead Bromide on Aluminum Alloys. Shell Aviation News, no. 144, June 1950, pp. 18-21.

10. Moore, D. G., Richmond, J. C., and Harrison, W. N.: High-Temperature Attack of Various Compounds on Four Heat-Resisting Alloys. NACA TN 1731, 1948.

TABLE 1.- REPRESENTATIVE COMPOSITIONS OF FIVE HEAT-RESISTANT ALLOYS

Alloy	Parts by weight of -							
	C	Cr	Ni	Co	Mo	W	Cb	Fe
Inconel	0.05	14	78	--	---	---	---	7
S-816	.4	20	20	44	4	4	4	3
H.S. 21	.2	28	2.5	62	5.5	---	---	1
AISI Type 347	.08	18	10	--	---	---	.8	71
19-9DL	.2	19	9	--	2	1.2	---	67



TABLE 2.- COMPOSITION AND APPLICATION DATA FOR

CERAMIC COATINGS A-19, A-417, AND A-520

(a) Coating compositions.

Ingredient	Parts by weight in -		
	A-19	A-417	A-520
Frit 1	50.0	----	------
Frit 11	50.0	----	------
Frit 331	-----	70.0	90.0
Chromic oxide	-----	30.0	------
Cupric oxide	-----	----	10.0
Black cobalt oxide	1.0	----	------
Calcined alumina	25.0	----	------
Enameling clay	10.0	5.0	6.0
Citric acid	.05	----	------
Sodium nitrite	-----	----	.025
Water	50.0	48.0	45.0

(b) Application data.

Specifications	Coating		
	A-19	A-417	A-520
Milling fineness[a]	1.0	0.4	0.3
Specific gravity of slip for dipping	1.60-1.62	1.78-1.82	1.85-1.90
Recommended fired thickness, mils	2-3	1.5-2.5	1.5-2.5
Firing temperature, °F	[b]1650	1850	1750

[a]Grams on a No. 200 U. S. Standard Sieve using a 50-ml sample of slip.

[b]Firing temperature of 1600° F recommended for application to low-carbon steel.

(c) Computed oxide composition of frits.

Oxide	Percent by weight in -		
	Frit 1	Frit 11	Frit 331
SiO_2	40.9	49.2	38.0
Al_2O_3	7.7	7.7	----
B_2O_3	17.5	17.4	6.5
Na_2O	15.3	15.2	----
K_2O	4.5	4.5	----
BaO	----	----	44.0
CaO	8.4	2.9	4.0
ZnO	----	----	5.0
BeO	----	----	2.5
F_2	3.5	.4	----
CoO	.6	.6	----
NiO	.5	.7	----
MnO_2	1.2	1.4	----
	100.1	100.0	100.0

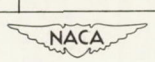


TABLE 3.- AVERAGE LOSS IN THICKNESS AT 1350°, 1500°, AND 1650° F FOR FIVE ALLOYS, BOTH WITH AND WITHOUT COATINGS, AFTER 6 HOURS OF HEATING IN AN AIR ATMOSPHERE CONTAINING $PbBr_2$ VAPOR

Alloy	Coating	Average loss in thickness in mils at -		
		1350° F	1500° F	1650° F
Inconel	None	[a]1.6	[a]6.2	[a]1.6
	Oxide	[a].9	[a]4.4	[a]1.5
	A-417	.4	.3	.4
	A-520	0	0	.6
	A-19	0	.2	.4
AISI Type 347	None	9.1	9.8	8.4
	Oxide	8.4	8.9	10.8
	A-417	0	.2	.2
	A-520	.2	.5	.2
	A-19	0	.2	0
S-816	None	1.2	6.6	2.5
	Oxide	1.9	6.3	2.1
	A-417	0	.5	1.0
	A-520	0	.6	.9
	A-19	.4	.8	.8
H.S. 21	None	3.7	3.5	2.4
	Oxide	2.5	2.2	1.5
	A-417	.1	1.0	.3
	A-520	0	.5	.6
	A-19	.2	.6	.5
19-9DL	None	9.9	10.1	10.2
	Oxide	5.8	8.1	10.7
	A-417	.4	1.1	1.0
	A-520	0	.7	.3
	A-19	.2	.5	.5

[a]Average of six specimens, all other values are averages of two specimens.

TABLE 4.- SPECTROCHEMICAL ANALYSES FOR LEAD IN BOTH SCALE LAYER AND UNDERLYING SURFACES OF UNCOATED ALLOYS AFTER 6 HOURS' HEATING AT 1500° F IN AN AIR ATMOSPHERE CONTAINING $PbBr_2$ VAPORS

Alloy	Estimated lead content	
	Scale (percent by weight) (1)	Alloy surface (2) (3)
Inconel	0.001 - 0.01	Lead detected
AISI Type 347	.001 - 0.01	Do.
19-9DL	.001 - 0.01	Do.
H.S. 21	.1 - 1.0	Do.
S-816	.1 - 1.0	Do.

[1]Sample used for analysis consisted of the scale that was removed from specimen after cooling.

[2]Alloy surface cleaned of all visible scale by a light sandblast.

[3]Impossible to estimate relative amounts of lead by methods used.

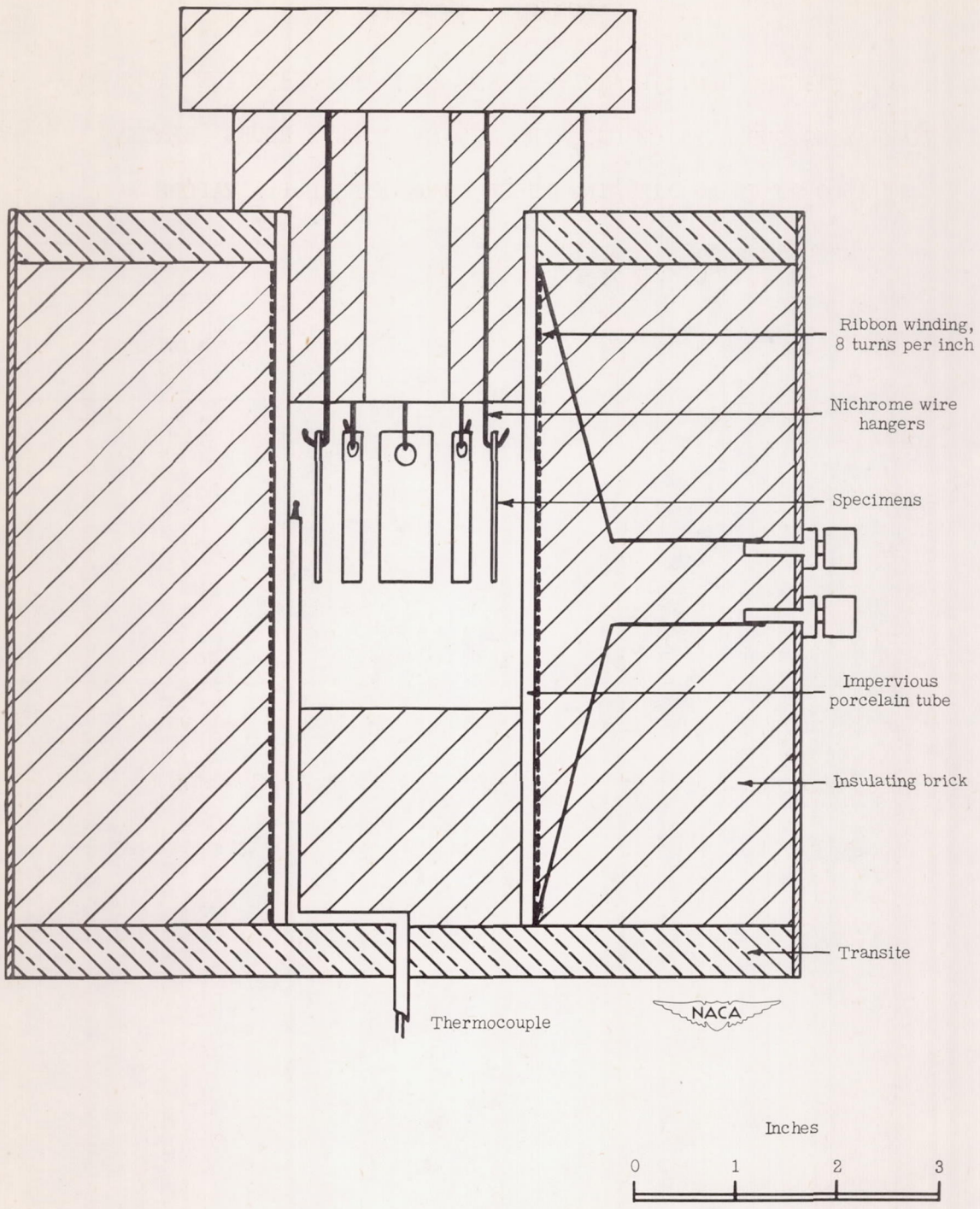


Figure 1.- Diagrammatic sketch of furnace equipment used for exposure of coated and uncoated alloy specimens to corrosive attack of $PbBr_2$ vapors in an air atmosphere at elevated temperatures. The $PbBr_2$ was introduced into the furnace at 1-hour intervals by placing it on the bottom insulating block without allowing it to touch specimens.

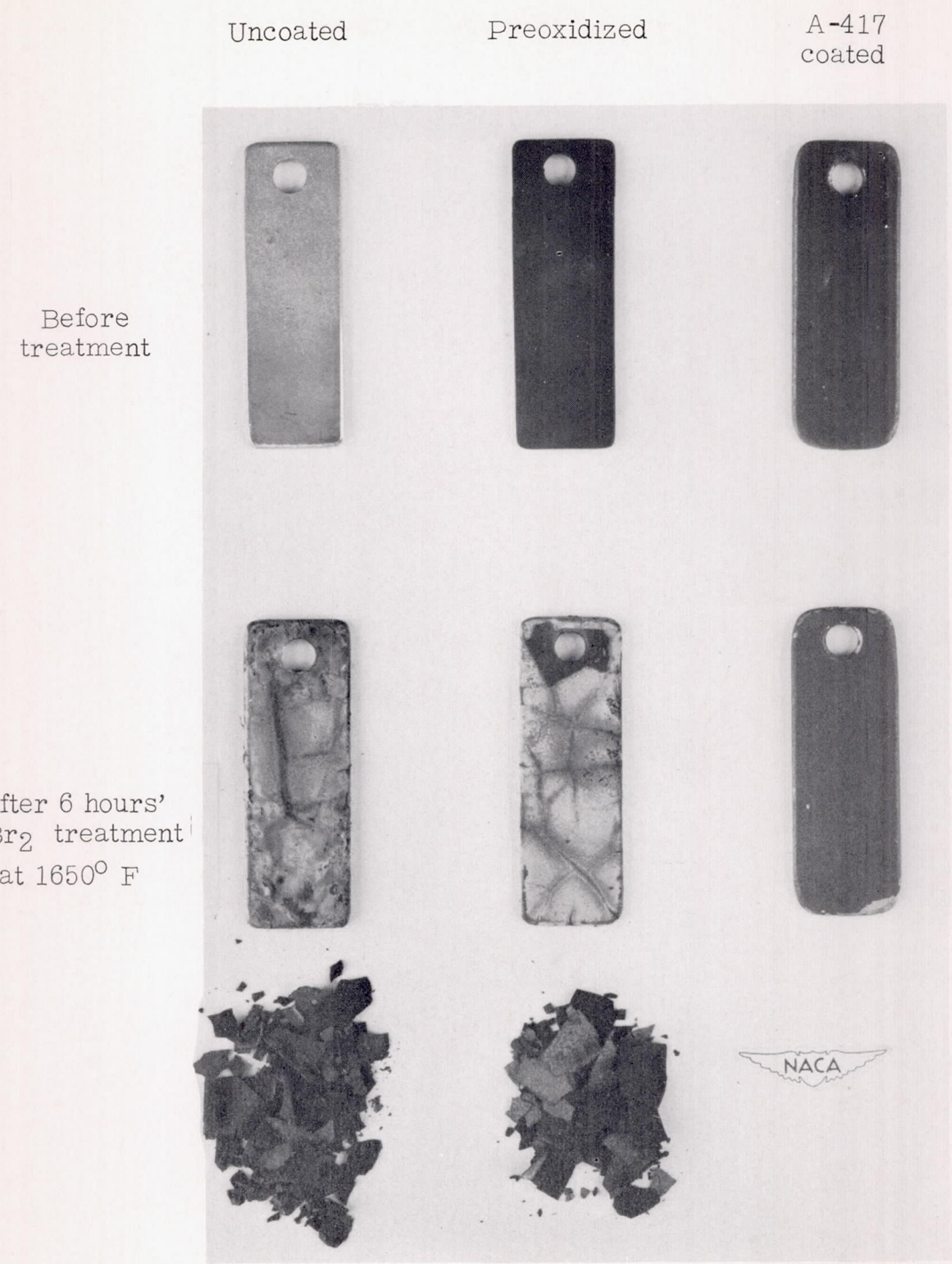


Figure 2.- Appearance of uncoated, preoxidized, and A-417 coated specimens of AISI Type 347 stainless steel before and after 6-hour $PbBr_2$ treatment at 1650° F. Scale that dropped off of uncoated and preoxidized specimens after treatment is shown at bottom of photograph. Mild flaking near edges of specimen coated with A-417 occurred after cooling and is believed to have been caused by initially imperfect coverage on these areas.

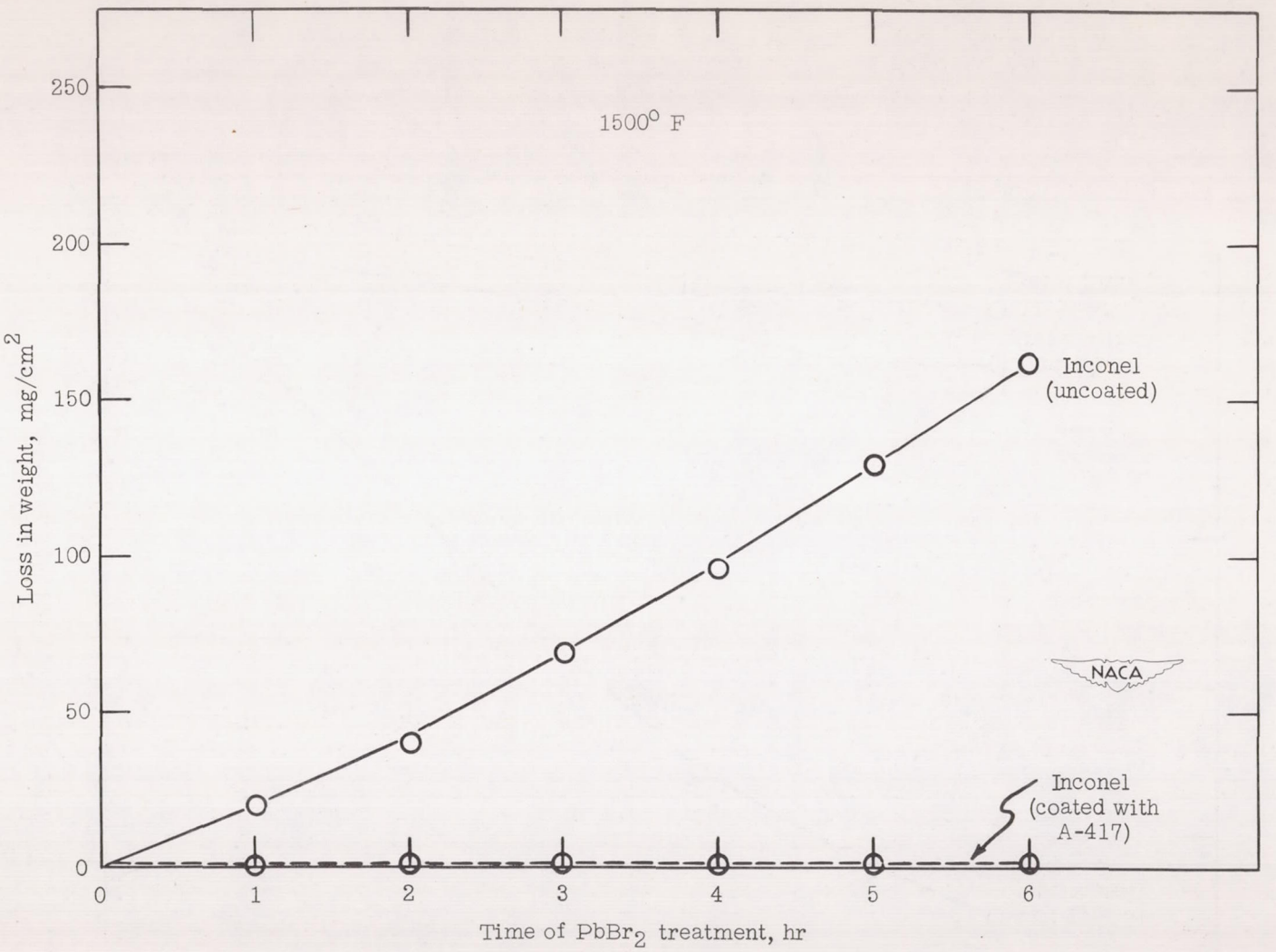


Figure 3.- Loss in weight against treatment time for coated and uncoated specimens of Inconel when exposed to $PbBr_2$ vapor in an air atmosphere at 1500° F.

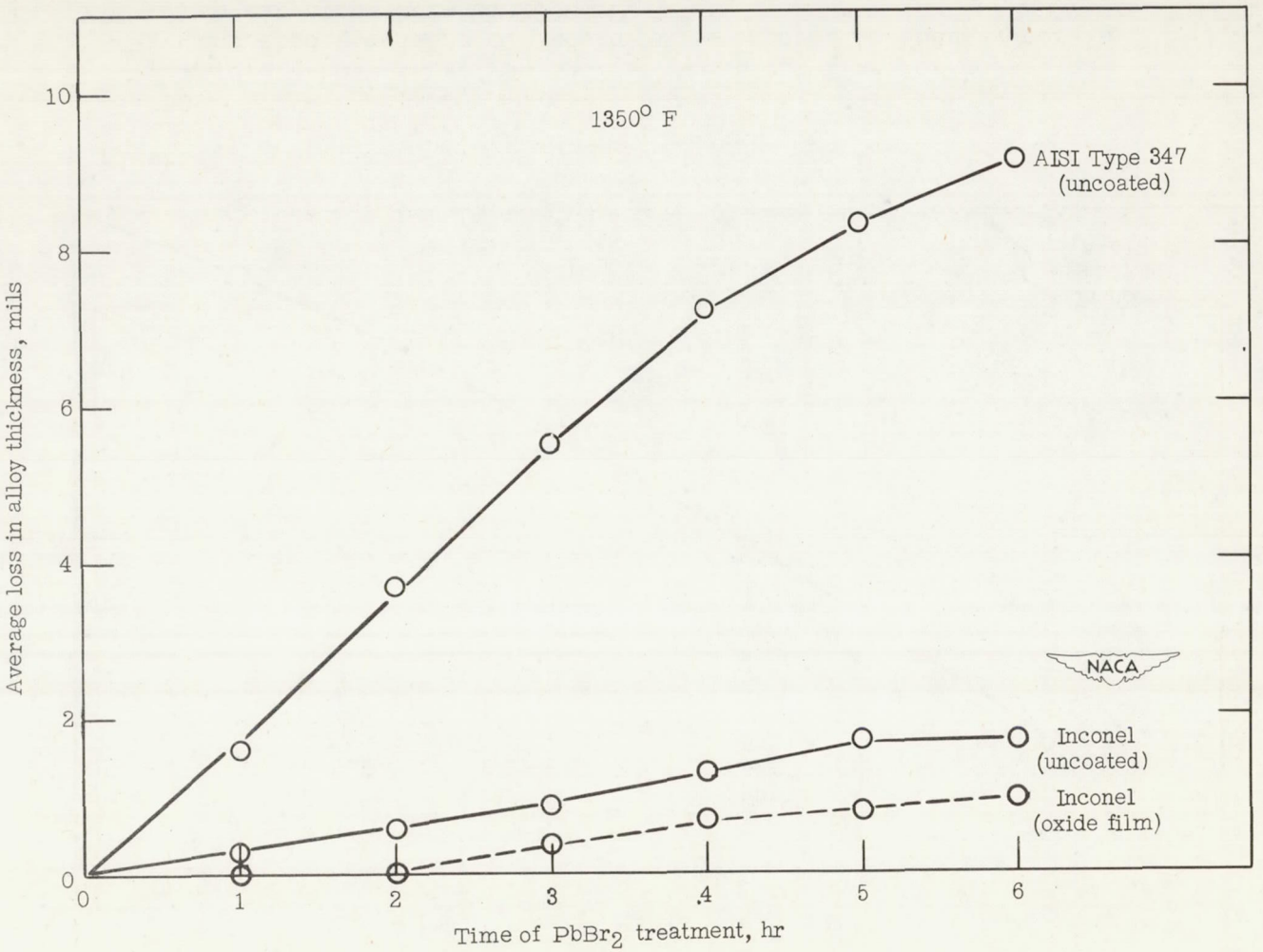


Figure 4.- Average loss in thickness against treatment time for AISI Type 347 stainless steel and Inconel when exposed to $PbBr_2$ vapors in an air atmosphere at 1350° F. The lower curve is for Inconel which had been preoxidized by heating in air for 4 hours at 1350° F.

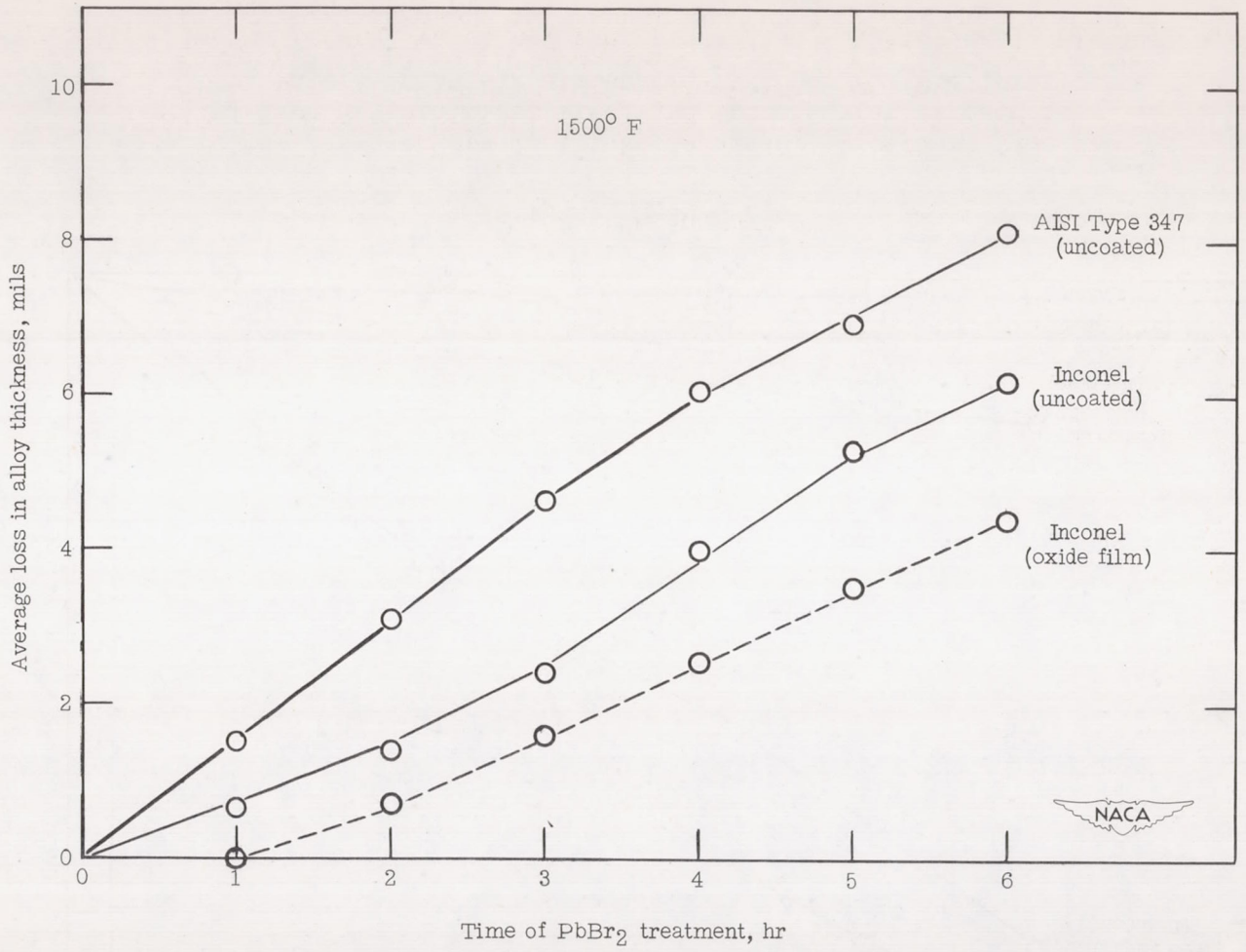


Figure 5.- Average loss in thickness against treatment time for AISI Type 347 stainless steel and Inconel when exposed to $PbBr_2$ vapors in an air atmosphere at 1500° F. The lower curve is for Inconel which had been preoxidized by heating in air for 4 hours at 1500° F.

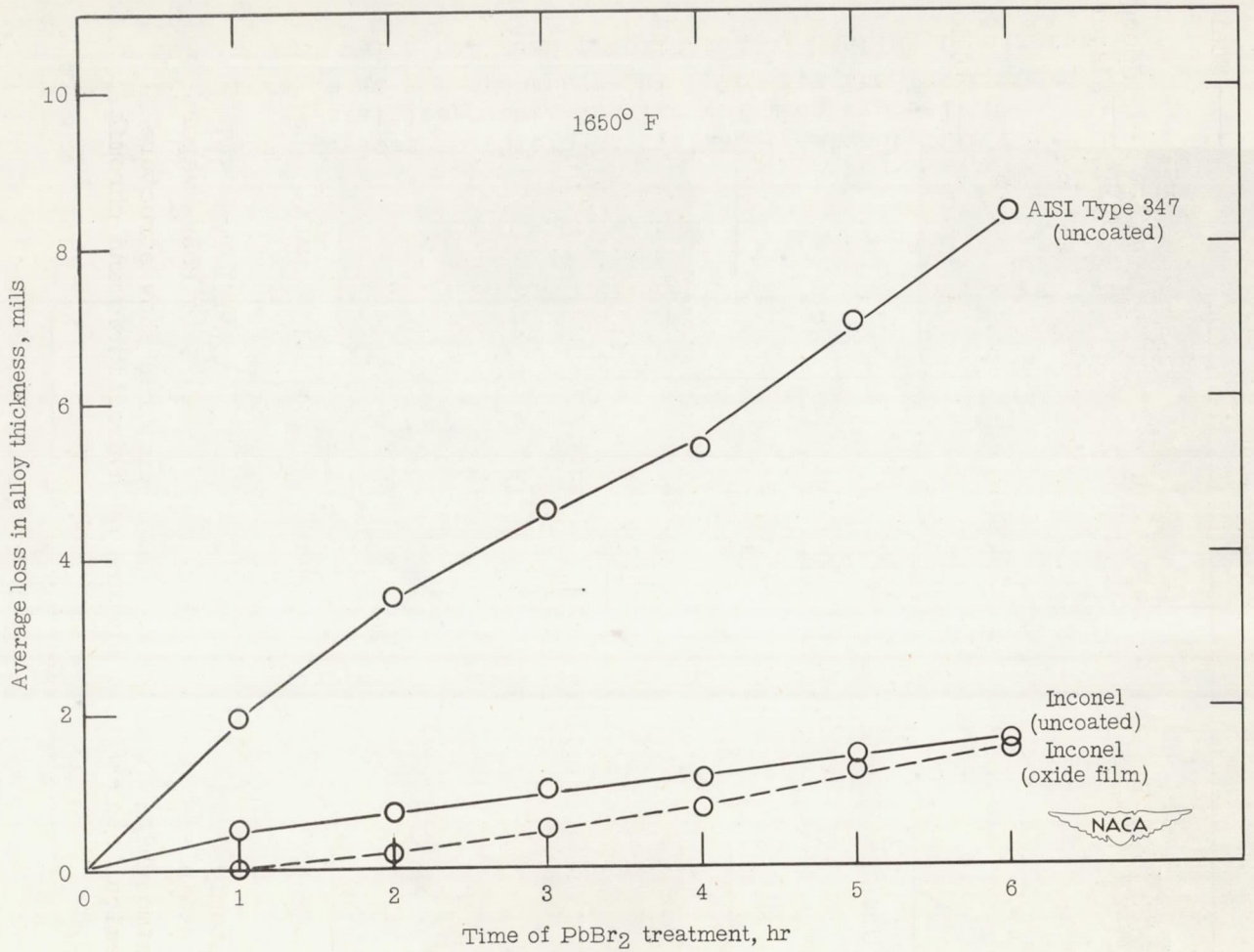


Figure 6.- Average loss in thickness against treatment time for AISI Type 347 stainless steel and Inconel when exposed to $PbBr_2$ vapors in an air atmosphere at 1650° F. The lower curve is for Inconel which had been preoxidized by heating in air for 4 hours at 1650° F.

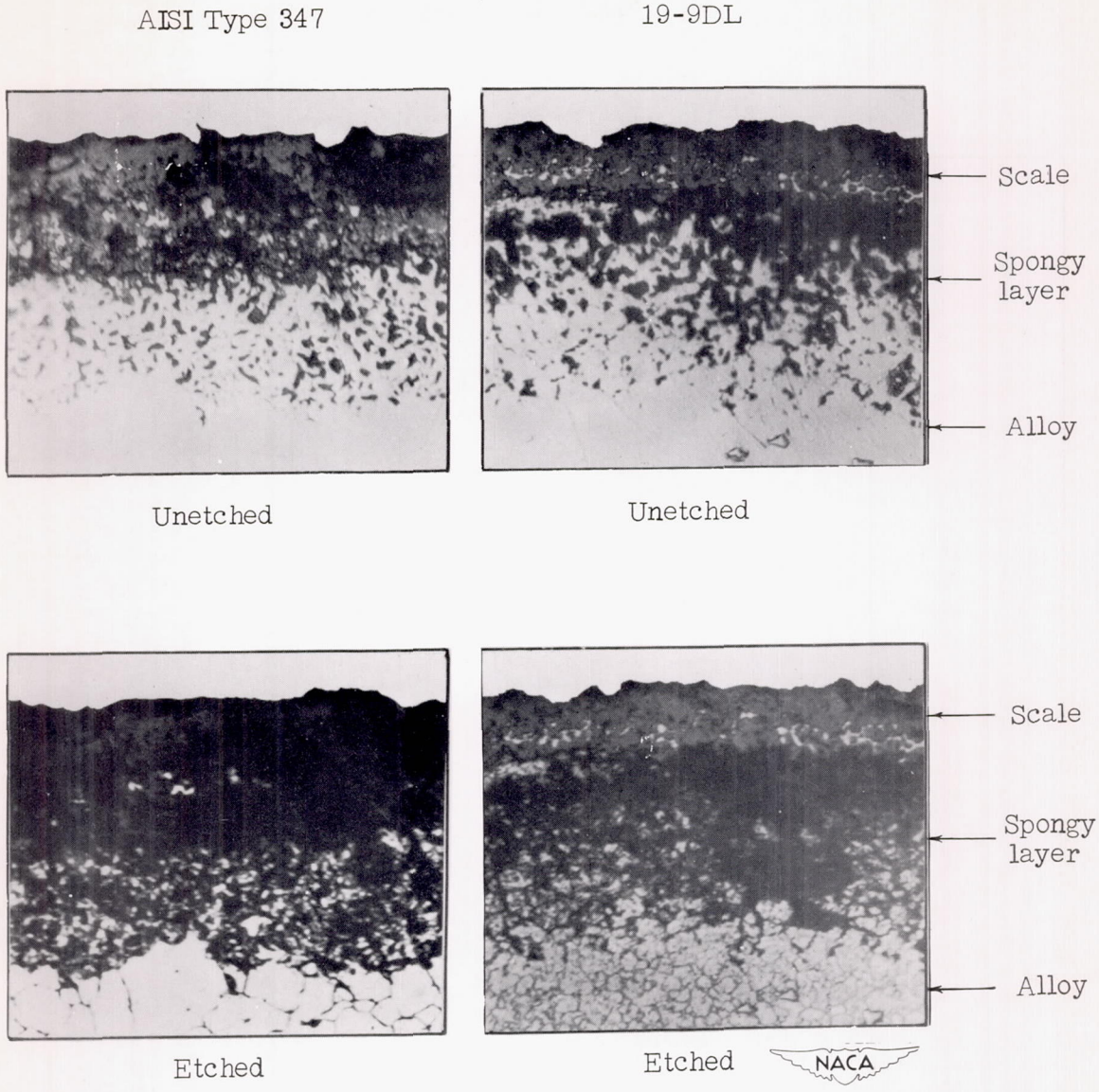


Figure 7.- Photomicrographs of uncoated specimens of AISI Type 347 and 19-9DL stainless steels after 6-hour exposure to $PbBr_2$ vapors in an air atmosphere at 1500° F. Lower pictures show structure after a chemical etch with a mixture of hydrochloric and chromic acids, X500.

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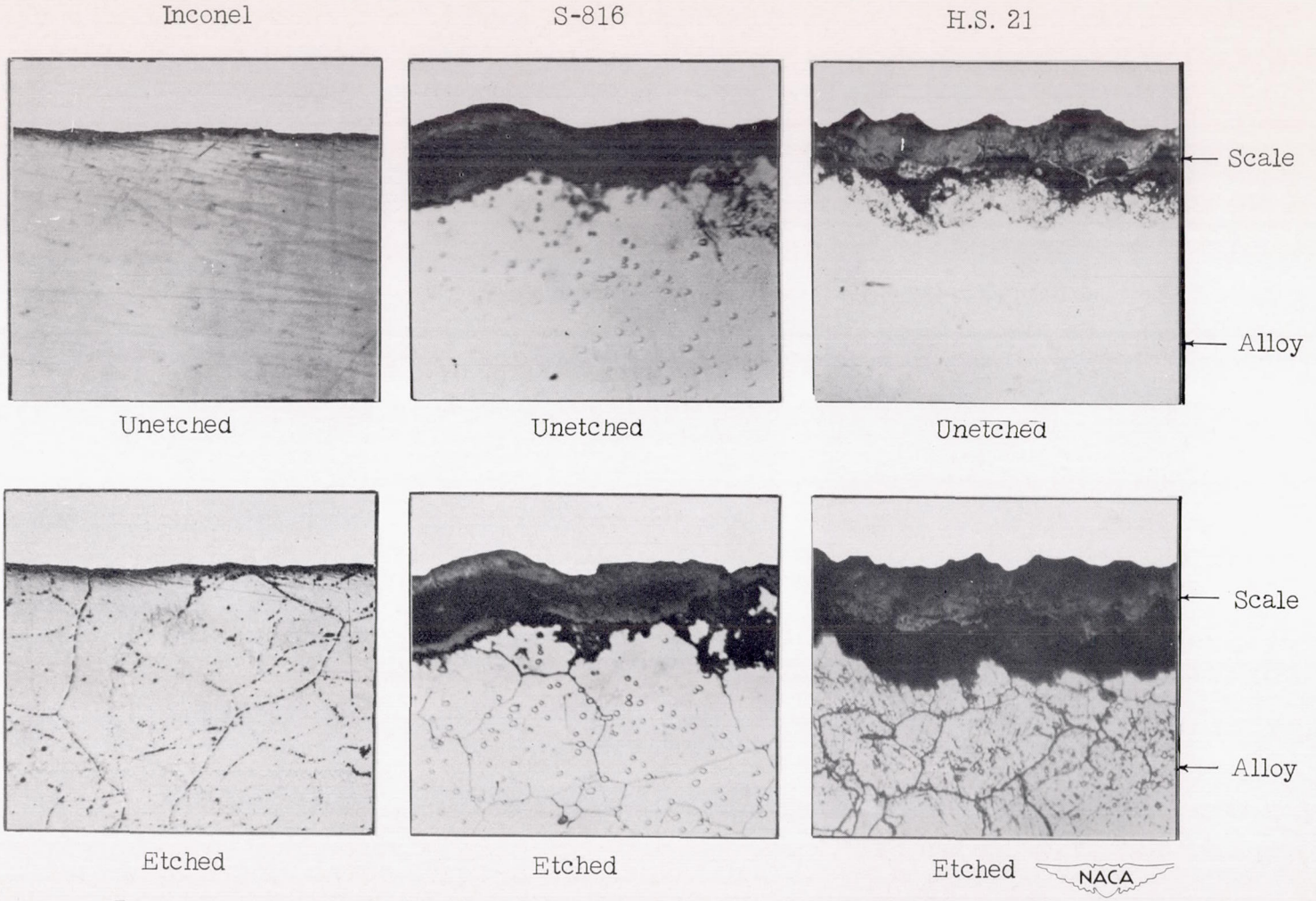


Figure 8.- Photomicrographs of uncoated specimens of Inconel, S-816, and H.S. 21 alloys after 6-hour exposure to $PbBr_2$ vapors in an air atmosphere at 1500° F. Lower pictures show structure of S-816 and H.S. 21 after an electrolytic etch with a mixture of hydrochloric and chromic acids and of Inconel after an electrolytic etch with oxalic acid. The scale formed on Inconel was nonadherent and fell off the specimens during cooling, X500.